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Novel Photo-Rearrangement of Oxime Methyl Ethers of 3-Acyl-1,2-dihydrocinnoline-*N*-phenyl-1,2-dicarboximides

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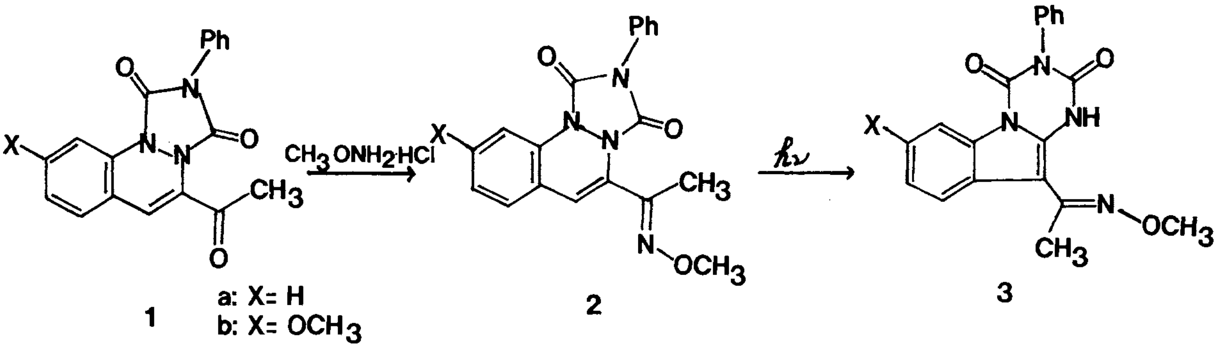
Irradiation of conjugated imino ethers containing an adjacent 1,2-diazadicarboximide group in benzene afforded rearranged indole derivatives (**3**) and a novel dimer in good yields. The latter was formed by nucleophilic attack of **3** to a dipolar intermediate.

In contrast to abundant information on photochemical reactivities of cyclic imides,1) only few reports concerning photochemistry of the aza homologue (1,2-diazadicarboximide) and the related compounds have been published, which include [4+2] and [2+2] cycloadditions2) ;di-π-methane rearrangement under sensitized conditions3) ; and transformation to triazine derivatives.4) Very recently, we have reported new synthetic methodology of heterocycles, using *N*-phenyl-1,2-diazadicarboximide derivatives (urazoles) **1** obtained from the reaction of benzylidene ketones with 4-phenyl-4*H*-1,2,4-triazole-3,5-dione(PTAD),5) and suggested that the diazadicarboximide ring should highly activate the adjacent carbon-carbon double bond.5,6) In the course of our study to explore utility of urazoles for syntheses of heterocycles, we found new photochemical reactions of urazoles **2**.

Irradiation of **2a** (0.29 mmol) in benzene (30 cm^3) for 8 h with a 400 W high-pressure mercury lamp through a pyrex filter resulted in loss of its characteristic green fluorescence. A conventional work-up gave unexpectedly a rearranged imino ether **3a** (89%, mp 242-244 ℃) containing an indole and a 1,3,5-triazine skeletons. The structure of **3a** was determined on the basis of spectral data, elemental analyses, and chemical



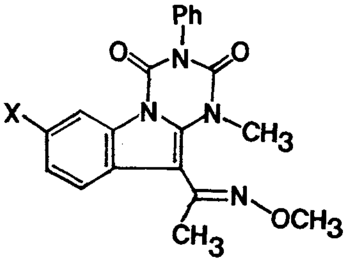
1 a: X= H
b: X= OCH3

2

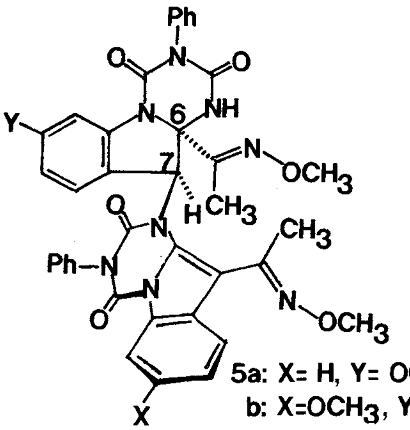
3

transformation. Its IR spectrum showed a characteristic band at 3445 cm^{-1} due to an amide group. A mass spectrum showed a peak at m/z 348(M$^+$) indicating **3a** to be an isomer of **2a**. The ^{1}H NMR spectrum of **3a** showed two methyl singlets at δ 3.93 and δ 2.40, and an amide proton at δ 10.0, which disappeared by addition of D_2O. A ^{13}C NMR spectrum also supported the proposed structure. **3a** was easily methylated with methyl iodide to afford **4a**,$^{7)}$ using a two phase system (aq $NaOH/CH_2Cl_2$/*n*-$(C_4H_9)_4NBr$).

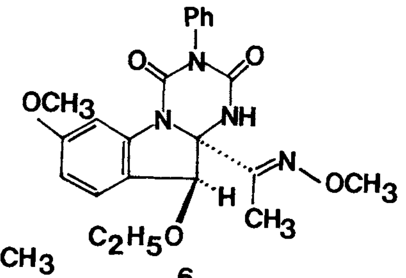
In contrast, more photosensitive **2b** possessing an electron-donating methoxy group aforded an intriguing compound **5b**(40%) together with the expected rearranged imino ether **3b**(21%) on irradiation for 1 h. The structure of **3b** was also confirmed on the basis of spectral data and elemental analyses.$^{8)}$ A mass spectrum of **5b** showed M$^+$ at m/z 756, which indicated a dimer structure. A ^{1}H NMR spectrum showed the presence of four methoxy and two methyl groups (δ 3.72, 3.80, 3.83, 3.92, 2.08 and 2.43), and a methine proton at 6.15(s, 7-H). A ^{13}C NMR spectrum showed a doublet at δ 64.3(C-7) and a singlet at δ 77.7(C-6) signals in addition to signals based on the skeleton of 3b. These and other spectral characteristics do not meet a cyclobutane structure arised from [2+2] cycloaddition.



4 a: X= H
b: X= OCH3



5a: X= H, Y= OCH3
b: X=OCH3, Y= OCH3



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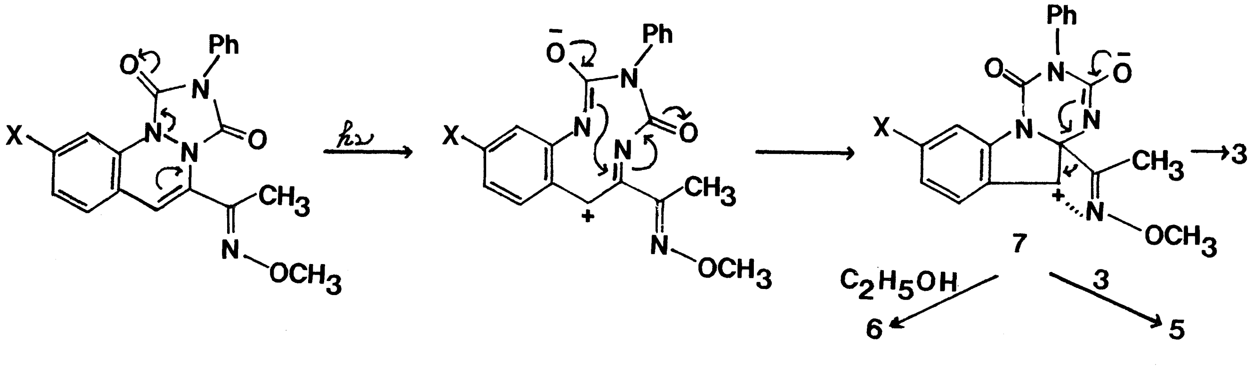
In order to confirm further the structure of this novel dimer (**5b**) and to elucidate the reaction mechanism, a photo-crossover experiment was performed using an equimolar mixture of **2b** and **3a** in benzene. Careful chromatographic separation of the product mixture afforded a crossover dimer **5a** together with the rearranged imino ether **3b** and the dimer **5b**. No reaction occurred in the dark and **3a** itself was quite stable under irradiation. Furthermore, irradiation of **2b** in benzene containing ethanol (1%) gave an ethanol-incorporated adduct **6** predominantly (no reaction in the dark). The structure of **6** was unambiguously determined by a single crystal X-ray analysis: Formula=$C_{22}H_{24}N_4O_5$, F.W.=424.46; orthorhombic,space group=Pbca,a=16.558(6),b=23.635(6),c=11.170(2)Å, $\alpha = \beta = \gamma = 90.00°$, V=4371.4(21)$Å^3$, Z=8, Dx=1.290 $g \cdot cm^{-3}$. The ^1H NMR and ^{13}C NMR of **5b** showed signals ascribable to the frameworks of **3b** and **6**. In addition, the stereochemistry of **5b** was determined as (6*S**,7*S**) by the analysis of NOESY spectrum which showed the NOEs between 7-H and the methyl proton of C-6 methoxyiminoethyl proton. These facts strongly supported the structure of **5b**.

The reaction mechanism will be most possibly explained by the following Scheme. A photochemical nitrogen-nitrogen bond cleavage in the diazadicarboximide moiety occurs through a polar excited state, and a transannular nucleophilic attack of the amide anion to the carbon-nitrogen double bond gives an intermediate **7** stabilized by participation by the imino group. The 1,2-shift of the methoxyiminoethyl group of **7** followed by prototoropy gives the indole derivative **3**. A nucleophilic attack of ethanol and **3** to **7** gives the corresponding triazines **6** and **5**. The results obtained from the photo-crossover experiment support the proposed mechanism. An alternative mechanism via aziridine$^{4)}$ cannot explain the rearrangement of the methoxyiminoethyl group.



Scheme

Thus the carbon-carbon double bond of the excited state of **2** should have a highly polar character caused by the diazadicarboximide group,9) and the methoxy group in the benzene ring and the imino group may stabilize it by its electron-donating ability.

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7) **4a**: mp 215-216 ℃ ; ^{1}H NMR (characteristic) δ 2.35(s,3H,CH_3), 3.57(s,3H,NCH_3), 4,02(s,3H,OCH_3); ^{13}C NMR (characteristic) δ 17.5(q), 33.3(q), 62.2(q), 98.5(s), 146.1(s), 148.9 (s), 149.8(s) ; IR (KBr) 1734, 1687 cm^{-1} ; MS: m/z 362(100%, M^+); HRMS: Found: 362.1376. Calcd for $C_{20}H_{18}N_4O_3$: 362.1380. The structure was unambiguously determined by a single crystal X-ray analysis, using **4b**. Crystal data: Formula= $C_{21}H_{20}N_4O_4$; monoclinic, space group= $P2_1/n$, a=8.728(2), b=10.664(5), c=19.106(3)Å, β =100.67(2)°, V=1747.7(10)Å^3, Z=4, Dx=1.377 g·cm^{-3}.

8) **3b**: mp 250-252 ℃ ; ^{1}H NMR δ 2.47(s,3H,CH_3), 3.83(s,3H,OCH_3), 4.00(s,3H,OCH_3), 7.13-7.93(m,8H,Ph), 10.0(bs,1H,NH); ^{13}C NMR (characteristic) δ 14.0(q), 55.7(q), 62.2(q), 93.7(s), 147.6(s), 153.4(s), 156.6(s); IR (KBr) 3265, 1742, 1700, 1634 cm^{-1} ; MS: m/z 378(100%, M^+); HRMS: Found: 378.1326. Calcd for $C_{20}H_{18}N_4O_4$: 378.1330.

9) Stokes shift of **2a** depended strongly on the polarity of solvents. This observation suggests that the excited state is highly polar; cf. J. R. Lakowicz, "Principles of Fluorescence Spectroscopy," Plenum Press, New York (1983).

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